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## Introduction

(19) **Expanded biopolymer-based articles and process of producing these**

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(0001) The invention relates to three-dimensional foamed articles of a biopolymer. The biopolymer can be obtained from renewable raw materials, in particular starch. The articles can be used as disposables, packaging or filling material, and have the added functionality of being biodegradable. The invention also relates to the production of such foamed articles.

(0002) Foam materials for disposable packaging purposes have the reputation of damaging the environment. Recycling of such materials has not, as yet, taken off to any significant degree, because of the low density (and therefore high transportation cost) of these materials. The use of biodegradable foam materials in these applications is therefore a sensible alternative. Furthermore, the possibility to produce a packaging from fully renewable resources will help to reduce the consumption of raw materials.

(0003) A characteristic of many biopolymers, in particular those based on starch, is their sensitivity to water. This is a disadvantage for packaging material where contact with water/food can be expected. Thus, there is a need for foamed packaging and similar materials made of a water-resistant biopolymer or provided with a water-resistant biodegradable coating.

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(0004) WO92/02559 describes a method for extruding and injection-moulding thermoplastic starch. The mouldings thus obtained have a high density, i.e. more than 1000 kg/m<sup>3</sup>, whereas 10-100 kg/m<sup>3</sup> is desirable for foam products for packaging, and in the case of thick-walled product entail high production costs (long cycle times).

(0005) EP 0 989 158 discloses a process for preparing foamed particles by degradable plastic material. This process consists of preparing foamed particles by expanding biodegradable plastic material, followed by submitting the particles to a heat treatment and/or to a treatment with a coating agent. Thus obtained particles are agglomerated to a foamed article by bringing the foamed particles into intimate contact with one another. A similar technique is disclosed in EP 0 594 977.

(0006) WO 99/57111 describes a mixture of materials that can be extruded to a water-resistant biodegradable foam. The extrudate can be used as loose-fill packaging material applied after, or preferably during or before the moulding step.

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Prior art

(57) Abstract: Three-dimensional foam mouldings made of a biodegradable thermoplastic polymer, in particular starch, and preferably a second biodegradable component can be manufactured in a discontinuous process by heating the polymer, in the form of an expandable bead or sheet or the like, in a mould having any desired shape under pressure in the presence of a blowing agent, and subsequently depressurising. The second component can be used to enhance the water-resistance of the mould product and can be applied after, or preferably during or before the moulding step.

(58) Title: EXPANDED BIOPOLYMER-BASED ARTICLES AND PROCESS OF PRODUCING THESE

(59) Abstract: Three-dimensional foam mouldings made of a biodegradable thermoplastic polymer, in particular starch, and preferably a second biodegradable component can be manufactured in a discontinuous process by heating the polymer, in the form of an expandable bead or sheet or the like, in a mould having any desired shape under pressure in the presence of a blowing agent, and subsequently depressurising. The second component can be used to enhance the water-resistance of the mould product and can be applied after, or preferably during or before the moulding step.

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or the extruded foam can be in the form of sheets which then can be thermoformed to desired articles.

[0007] US 6,030,673 (WO 96/05254) discloses a method for the preparation of moulded starch-bound containers and other articles. In this method a viscous mixture of 5 a starch-based binder, filler material, a solvent and possible other additives is prepared. This mixture is fed into an article-forming apparatus where the solvent is removed from the mixture by applying heat and a cellular structure is formed. According to DE 4228779 (WO 94/05492), a composite shell material can be produced by foaming a 10 50% starch suspension of starch on a pre-shaped cardboard sheet; the foamed product is intended for packaging and has a density of 190 kg/m<sup>3</sup>.

[0008] According to the methods known from the prior art, preparing foamed articles of biodegradable material involves complex mixtures of materials to achieve water resistance or complex and expensive articles forming machinery requiring a large capital investment. Moreover, it is difficult, if at all possible, to produce articles with any 15 desired three-dimensional shape using these known methods.

[0009] Therefore there is a need for a method that allows the production of water-resistant biopolymer-based foamed articles in any desired three-dimensional shape in an 20 economically feasible way. The object of the present invention is to provide such articles and a method for their preparation.

#### 20 *Description of the invention.*

[0010] A method has been found to manufacture truly three-dimensional biopolymer-based foamed articles. This method involves the manufacture in a rapid, discontinuous or semi-continuous process, of foamed articles by subjecting the biopolymer containing 25 a gassing agent to an elevated temperature and pressure, in a closed-off space, maintaining this situation for a certain period of time and followed by a rapid depressurisation causing the biopolymer to foam.

[0011] The biopolymer is foamed within a mould having vent holes and the desired 30 shape of the article, where the mould is enclosed in the closed-off space. The biopolymer can be provided with a water-resistant coating that either can be applied in the foaming process by foaming the biopolymer between water-resistant films or that can be applied afterwards.

[0012] The term biopolymer as used herein denotes three classes of polymers. Firstly, biopolymers include any polymer that can, as such, directly be extracted or otherwise

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isolated from renewable natural resources. Examples thereof are polysaccharides and polypeptides. Post-modification of the polysaccharides or proteins by chemical and/or physical means is considered to be comprised in this class of biopolymers. Secondly, biopolymers include polymers that are obtained by non-natural (i.e. industrial) polymerisation of natural monomers or oligomers, i.e. monomers or oligomers produced from renewable resources. Examples thereof include poly(lactic acid). Thirdly, biopolymers as used herein include polymers obtained by biotechnological production, possibly but not necessarily including genetic modification of production organisms, from natural resources. Examples thereof comprise polyhydroxyalkanoates produced by suitable micro-organisms. In addition, other biodegradable, synthetic polymers can be used. Examples thereof include aliphatic polyesters and polyester-amides, polycaprolactone and the like.

[0013] The biopolymers to be used in the present invention should be melt-processable when they are subjected to the heat and pressure treatment for the purpose of forming foamed mouldings. The melt-processability can be inherent to the particular biopolymer, for example in the case of poly(lactic acid) or polyhydroxyalcanoic acids, or it can be achieved by subjecting the biopolymer to a particular treatment, such as mixing with plasticisers, thermomechanical treatment, heating and the like. Preferably, the melt-processable polymer is in a solid form, e.g. granules, powder or sheets, containing less than 30% of water on the basis of total weight of the polymer as introduced into the foaming mould.

[0014] Particularly suitable as a melt-processable biopolymer is thermoplastic starch. This starch is derived, for example, from potatoes, peas, wheat, rice, maize or tapioca, and is used as such or mixed with other biodegradable polymers such as cellulose derivatives, other polysaccharides such as guar gum, locust bean flour, tragacanth, pectin, gum arabic or other gums, natural rubber, polyesters such as poly(caprolactone) and poly(lactic acid), proteins such as gluten and casein. Proteins and starch can also be added together in the form of flour. The other polymers can amount up to 75 wt % of the mixture.

[0015] The thermoplastic starch can be based on native starch or alternatively on physically or chemically modified starch and special starches resulting from natural selection and/or generic modification of starch-producing plants. Physically modified starch comprises inter alia starch modifications which are produced by ion exchange

(e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ ). Chemically modified starch and starch derivatives comprise oxidised, carboxymethylated, hydroxymethylated starch and starch derivatised in some other way.

[0016] The starch is preferably admixed with a plasticiser such as a polyol (glycol, diethylene glycol or another glycol or polyalkylene glycol, glycerol, glycerol monostear, and the like), citric acid ester or a sugar polyol (for example sorbitol, lactitol) or (oligo)saccharide (for example glucose, sucrose, maltose and oligomers such as inulin and maltodextrins), or urea, but water on its own may also be sufficient. The amount of water can be, for example, 2.5-40 w%, in particular 3-35 w% based on the total amount of polymer. The amount of additional plasticiser such as glycerol is preferably 0-25 w%, in particular 1-15 w% based on the total amount of polymer. The polymer can further be admixed with an emulsifier such as lecithin or a monoglyceride, a release

10019 The polymer is shaped into a form which makes it suitable for the foaming process. This form can be referred to as an expandable bead or sheet or other shape. This can be done by thermomechanical treatment, in particular by extrusion, during which blowing agents and other additives can be present. Extrusion can result into granules or pellets in accordance with granulating or pelleting processes known per se, for example by extrusion in a twin-screw extruder at elevated temperature (60-200°C, for example for starch-based biopolymers in particular 100-150°C). The size of the granules is determined by the granulation rate and any grinding steps after granulation and the size can be that small that the granules can be referred to as powder. Instead of granules, sheets obtained by extrusion can be suitable forms for the subsequent foaming process. The sheets can be made from the biopolymers as such, with optional process aids, but they can also be coextruded sheets with a second component as described

[0020] The biopolymer granules/powder obtained can be conditioned to a moisture content that is optimal for the process. Depending on the basic biopolymer and on the content of other plasticisers, the moisture content after conditioning varies between 5 and 30%, for example for a starch-based biopolymer between 5 and 20% and for a cellulose diacetate-based polymer between 3 and 15%. Prior to the foaming step, the granules/powder can be coated in order to improve their mutual adhesion and cohesive

[0017] Other biopolymers of the first class, such as cellulose, cellulose derivatives and proteins can similarly be transformed to a melt-processable polymer by addition of plasticisers and the like. Any of these biopolymers may be admixed with other, preferably (bio)degradable polymers such as polyvinyl acetate, polyvinyl alcohol, copolymers thereof with ethylene (EVOH), at a rate of up to e.g. 50%, preferably 0-30 % by weight of the other polymer.

[0018] The biopolymer is admixed with a blowing agent. Physical blowing agents such as low-boiling solvent and low-boiling plasticisers referred to above, in particular water or lower alcohols, or chemical blowing agents, e.g. azodicarbonylic esters or amides or benzene-sulphonamide N-phenyl-hydrazide or a metal bicarbonate can be used as a blowing agent. Amounts can range from 1 to about 30% with respect to the total amount of biopolymer and plasticiser. The blowing agent can be added before or after the addition of further components such as plasticisers.

[0021] The biopolymer granules/powder obtained are transferred to a mould, and foamed in the mould which has the shape of the desired article (referred to as product mould). The product mould is preferably enclosed in a larger closed-off space (referred to as foam mould). The mould cavity of the foam mould is connected to the outside environment through an outlet valve, being closed at the beginning of the process. The product can also be introduced into the foam mould by injection moulding. The foam mould is heated to the process temperature by continuous heating through injection of a flow of superheated steam or hot air or by continuous external heating or microwave heating of the foam mould until the internal temperature has attained the required temperature. In case of continuous heating, the superheated steam and/or hot air have a temperature, pressure and humidity adapted to the desired processing conditions in the foam mould. The processing conditions depend on the biopolymer being foamed and can range from 100 to 220°C and from 1 to 50 bar.

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[0022] It can be beneficial to further increase the pressure in the mould. This can be done by applying an elevated initial pressure or by adding an additional amount of blowing agent in the mould. The pressure build-up prevents the boiling and subsequent evaporation of the blowing agent contained in the biopolymer. After a certain amount of time, the cavity of the foam mould is rapidly depressurised. This depressurisation causes an instantaneous gasification of the blowing agent followed by expansion of the biopolymer to a foamed article constrained by the physical boundaries of the product mould. The final article preferably has a density of  $0.10\text{ kg/m}^3$ .

[0023] Advantageously, the foamed biopolymer is provided with a water-resistant coating, in case the biopolymer itself is not sufficiently water-resistant in view of the intended use of the moulded biopolymer. The water-resistant coating can consist of a second biodegradable component, which can be a biopolymer from one of the three classes of biopolymers as defined above. Such biopolymer can be made more water-resistant, if necessary, by derivatisation, such as esterification or etherification, e.g. in the case of starch or cellulose or another polysaccharide. In addition, other synthetic polymers or oligomers or waxes, preferably biodegradable, can be used as component for a water-resistant coating. Examples thereof include aliphatic polyesters and polyester-amides, polycaprolactone and the like. The final properties of the coating can be obtained by a final curing or cross-linking step.

[0024] There are several possible ways for applying the coating of the second component. Firstly, the coating can be applied during foaming (referred to as in-situ coating). In-situ coating can be done by separately introducing the second component into the product mould as a film or lining. When the biopolymer is foamed, the expanding foam will take the shape of the product mould, while simultaneously shaping the film and adhering to it. Secondly, this principle can be used by foaming a coextrudate of the biopolymer and the second component, e.g. in the form of a laminated sheet. In this way, adhesion between biopolymer and coating has been established before foaming. Thirdly, a coating can be applied by known means, e.g. dipping or spraying. This can be done with the biopolymer granules before foaming or with the foamed article after foaming. If required, a tie layer or adhesive layer can be used to improve the adhesion of the coating to the polymer.

[0025] The process of the invention is a discontinuous or semi-continuous process. The mould to be used can have any desired shape, depending only on the shape of the

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polymer articles to be produced. Therefore, the heating and pressurising/depressurising steps of the process are different from extrusion foaming processes which do not allow freedom of shape in the articles produced.

**Example 1**

5 [0026] Native potato starch, containing about 17 wt% of water, was made into melt-processable granules of about 3 mm diameter by extrusion under addition of water (about 20 wt%) and subsequent pelletisation of the extrudate. The extruded thermoplastic starch granules were conditioned to a water content of 10-15 wt%. The conditioned granules were brought into a product mould and the filled product mould 10 was placed in a steam mould and pressurised to 3 bar. A steam flow having a temperature of 190°C was used to heat the foam mould. The steam flow was maintained for 5 minutes, resulting in an internal temperature of the foam mould of 185°C. Simultaneously with discontinuing the steam flow, the foam mould was rapidly depressurised, causing the starch granules to expand to a foam. The resulting foam had a density of about  $20\text{ kg/m}^3$ , consisted of closed cells, and had a homogeneously distributed cell size and shape with an average cell size ranging from 0.1 to 0.5 mm. Mechanical properties include a resiliency of 65%.

Steam  
at which 5 min  
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[0027] It will be appreciated that the invention is not limited to the specific examples described above. Various modifications and variations will be apparent to those skilled in the art without departing from the scope and spirit of the invention. The invention is intended to cover all such modifications and variations.

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## Claims

1. A process of producing a foam moulding made of a biopolymer, characterised in that the biopolymer is, or is transformed to a melt-processable polymer, and is heated in a mould having any desired three-dimensional shape under pressure in the presence of a blowing agent and subsequently is depressurised, said heating under pressure and depressurising being discontinuous.

2. A process according to Claim 1, wherein the biopolymer comprises starch, cellulose or a protein, or a derivative of starch, cellulose or a protein.

3. A process according to Claim 2, wherein the biopolymer is transformed to a melt-processable polymer by subjecting it to a thermomechanical treatment.

4. A process according to Claim 3, wherein the thermomechanical treatment is carried out in the presence of a plastisiser such as a polyol.

5. A process according to any one of Claims 1-4, wherein the biopolymer, prior to said heating under pressure, is brought in a form suitable for foaming by extrusion to granules or sheet.

6. A process according to any one of Claims 1-5, wherein the melt-processable biopolymer, prior to said heating under pressure, contains between less than 30 wt%, preferably between 3 and 20 wt.% of water.

7. A process according to any one of Claims 1-6, wherein said heating under pressure is carried out at a temperature between 100 and 220°C and at a pressure between 1 and 50 bar.

8. A process according to any one of Claims 1-7, wherein a second component is coated onto the melt-processable polymer before or after said heating under pressure or before or after said depressurising.

9. A process according to Claim 8, wherein the second component comprises a starch derivative, a cellulose derivative, a polyester such as poly(lactic acid) or another poly(hydroxyalcanoic acid), or a copolyester such as a polyester amide.

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10. A process according to Claim 8 or 9, wherein the second component and the biopolymer are co-extruded prior to said heating under pressure.

11. A process according to Claim 8 or 9, wherein the second component and the biopolymer are separately introduced into the mould and are simultaneously subjected to the heating under pressure.

12. A process according to Claim 8 or 9, wherein the second component is coated on the foamed moulding.

13. A moulding of a foamed biopolymer, obtainable by means of the process according to any one of the preceding claims.

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## INTERNATIONAL SEARCH REPORT

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